JOC The Journal of Organic Chemistry

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Rhodium- and Iridium-Catalyzed Dehydrogenative Cyclization through Double C−H Bond Cleavages To Produce Fluorene Derivatives

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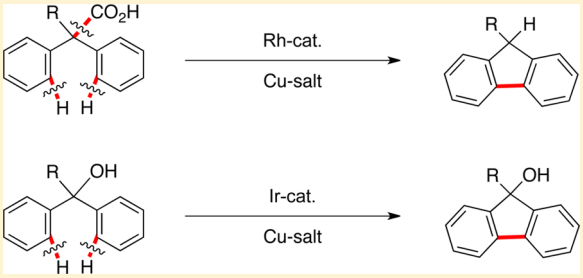
Supporting Information

ABSTRACT: The rhodium-catalyzed cyclization of a series of 2,2-diarylalkanoic acids in the presence of copper acetate as an oxidant smoothly proceeded through double C−H bond cleavages and subsequent decarboxylation to produce the corresponding fluorene derivatives. The direct cyclization of triarylmethanols also took place efficiently by using an iridium catalyst in place of the rhodium, while the hydroxy function was still intact.



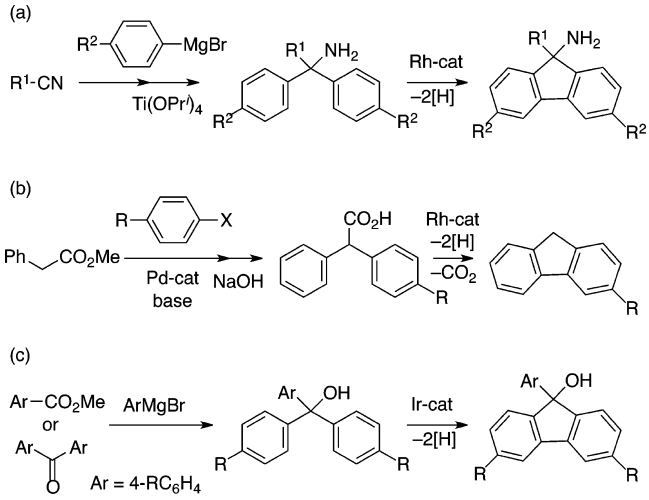
INTRODUCTION

The transition-metal-catalyzed aryl−aryl coupling between aryl halides and arylmetal reagents has been recognized as one of the most reliable methods for constructing biaryl frameworks, which can be ubiquitously seen in a wide range of fine chemicals including medicines and organic materials.[1] From atom- and step-economical points of view, the direct coupling of simple arenes through Ar−H bond cleavage has recently attracted much attention because waste(s) from the coupling event as well as the substrate preparation steps can be undoubtedly reduced.[2] In particualr, the dehydrogenative coupling of two simple arenes involving double Ar−H bond cleavages has been regarded as a challenging goal in the field of cross-coupling.[3] However, examples actually applied to precise organic synthesis are so far limited due to difficulties in controlling regioselectivity in the C−H bond activation steps and avoiding undesired homocouplings.

Meanwhile, the intramolecular version of the dehydrogenative aryl−aryl coupling may provide useful synthetic procedures for dibenzo-fused cyclic compounds.[3h,4] This type of reaction has been undertaken only under palladium(II) catalysis, and therefore, the substrate scope is quite limited. Recently, various rhodium(III)-catalyzed dehydrogenative functionalization reactions of Ar−H bonds have been developed by us[5] and others[6] to demonstrate a wider range of applicability compared to that of palladium(II)-based catalyzes, and we succeeded in applying the Rh(III) catalysis to an intramolecular dehydrogenative cyclization. Thus, 1-amino-1,1-diarylalkanes were found to be effectively transformed to 9-aminofluorenes (Scheme 1a).[7] Since the starting amines can be readily prepared by 2-fold nucleophilic addition of arylmagnesium reagents to nitriles,[8] this reaction provides a simple and useful approach from the easily available substrates to the cyclized products. Notably, fluorene derivatives have been employed as important components in organic materials fields including light-emitting devices, organic field-effect transistors, and organic photovoltaic cells as well as biosensors.[9]

2,2-Diarylacetic acids and triarylmethanols can also be readily prepared though the arylation reactions of phenylacetates and

Scheme 1. Fluorene Synthesis from Simple Building Blocks



Received: January 9, 2013
Published: January 29, 2013

   dx.doi.org/10.1021/jo4000465 | J. Org. Chem. 2013, 78, 1365−1370

benzoates or benzophenones, respectively (Scheme 1b,c). It might be conceived that these substrates undergo similar dehydrogenative cyclization, as the oxygen-containing functionalities may act as good directing groups as well as amine- and imine-based ones to enable catalytic regioselective C−H bond functionalization. Indeed, we observed that 2,2-diphenylacetic acid as well as 2,2-diphenylpropanoic acid could undergo rhodium-catalyzed direct cyclization accompanied by decarboxylation.[10] Consequently, the scope of the reactions with the acid derivatives has been investigated. On the other hand, triarylmethanols have been found to give rise to the corresponding fluorenes with the hydroxy function intact. It should be noted that 9-hydroxyfluorene structures have been utilized as the core of crystalline inclusion compounds[11] and luminescent materials[12] as well as the sources of stable 9-fluorenyl radicals and cations.[13] Interestingly, the reaction of the alcohols is effectively catalyzed by iridium rather than rhodium. The detailed results for these oxygen-directed dehydrogenative cyclization reactions are described herein.

RESULTS AND DISCUSSION

Rhodium-catalyzed oxidative coupling reactions on arenes are commonly carried out by using $[Cp^*RhCl_2]_2$ as the catalyst precursor in combination with a Cu(II) or Ag(I) oxidant (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl). We previously found that the oxidative cyclization of 2,2-diphenylpropanoic acid (**1a**) could be better catalyzed by $[Cp^ERhCl_2]_2$[14] rather than $[Cp^*RhCl_2]_2$ (Cp^E = 1,3-bis(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl).[7] Thus, treatment of **1a** in the presence of $[Cp^ERhCl_2]_2$ (2 mol %), $AgSbF_6$ (8 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2 equiv), and K_2CO_3 (1 equiv) in diglyme at 120 °C for 20 h afforded the expected fluorene **2a** in 65% GC yield (Table 1, entry 2 vs entry 1 with $[Cp^*RhCl_2]_2$). The yield was improved up to 73% (63% after isolation) by adding 2,6-dimethylbenzoic acid (0.5 equiv) as a promoter (entry 3).[15] Under similar conditions, 2-methoxy-2,2-diphenylacetic acid (**1b**) also underwent the reaction efficiently to produce 9-methoxyfluorene (**2b**) selectively (entry 4). In the reaction of 2,2-diphenylacetic acid (**1c**), a slightly better result was obtained at 100 °C rather than at 120 °C (entry 5 vs entry 6). Thus, under the milder conditions, 9-unsubstituted fluorene (**2c**) was obtained in 56% yield. In this case, the addition of 2,6-dimethylbenzoic acid was not necessary (entry 7). Treatment of 2-(4-substituted phenyl)-2-phenylacetic acids **1d−g** under similar conditions gave the corresponding 3-subtituted fluorenes **2d−g** in 43−56% yields (entries 8−11). In contrast to **1d−g**, treatment of substrates possessing electron-withdrawing groups including halogens gave only trace amounts of cyclization products. Most of the substrates were consumed by unidentified side reactions. Five-membered ring formation exclusively took place upon treatment of 2-(1-naphthyl)-2-phenylacetic acid (**1h**) to produce *11*H-benzo[*a*]fluorene (**2h**) (entry 12): no six-membered cyclic product via C−H bond cleavage at the C8-position of the naphthyl moiety was detected. Similarly, 2-(2-naphthyl)-2-phenylacetic acid (**1i**) underwent the reaction to produce *11*H-benzo[*b*]fluorene (**2i**) (entry 13). No regioisomer was detected by GC and GC−MS even in this case. Under the present conditions, 2-(2 or 3-thienyl)-2-phenylacetic acid remained almost completely intact. The construction of ladder-type indenofluorene structure was achieved through double cyclization of *α*,*α*′-diphenyl-1,4-benzenediacetic acid (**1j**), albeit with low efficiency (entry 14).

Table 1. Reaction of 2,2-Diarylalkanoic Acids 1[a]

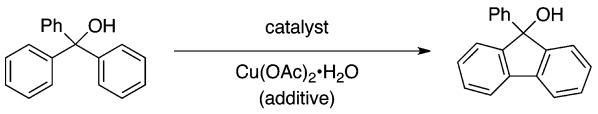
entry	1	temp (°C)	time (h)	product, % yield
1[b]	**1a**, R = Me	120	20	**2a**, R = Me, (45)[c]
2	**1a**, R = Me	120	20	**2a**, R = Me, (65)[c]
3[d]	**1a**, R = Me	120	20	**2a**, R = Me, 63 (73)[c]
4[d]	**1b**, R = OMe	120	20	**2b**, R = OMe, 62
5[d]	**1c**, R = H	120	20	**2c**, R = H, (51)[c]
6[d]	**1c**, R = H	100	48	**2c**, R = H, (56)[c]
7	**1c**, R = H	100	48	**2c**, R = H, 57 (57)[c]
8	**1d**, R = Me	100	48	**2d**, R = Me, 56
9	**1e**, R = Bu^t	100	48	**2e**, R = Bu^t, 53
10	**1f**, R = 4-Bu^{t}C$_6$H$_4$	100	48	**2f**, R = 4-Bu^{t}C$_6$H$_4$, 45
11	**1g**, R = OMe	100	48	**2g**, R = OMe, 43
12	**1h**	100	48	**2h**, 50
13	**1i**	100	48	**2i**, 33
14	**1j**	100	48	**2j**, 14

[a]Reaction conditions: [**1**]:[{Cp^ERhCl_2}$_2$]:[$AgSbF_6$]:[$Cu(OAc)_2{\cdot}H_2O$]:[K_2CO_3] = 0.5:0.01:0.04:1:0.5 (in mmol), in diglyme (3 mL) under N_2. [b]$[Cp^*RhCl_2]_2$ (0.01 mmol) was employed in place of $[Cp^ERhCl_2]_2$. [c]GC yield. [d]2,6-$Me_2C_6H_3CO_2H$ (0.25 mmol) was added.

We next examined the cyclization of triphenylmethanol (**3a**). First, **3a** was treated under similar conditions to those for the reactions of 1-amino-1,1-diarylalkanes in Scheme 1a,[7] using $[Cp^ERhCl_2]_2$ or $[Cp^*RhCl_2]_2$ (2 mol %) together with $Cu(OAc)_2{\cdot}H_2O$ (2 equiv) in *o*-xylene at 130 °C. However, no cyclized product was obtained at all (entries 1 and 2 in Table 2). When the reaction was conducted with the addition of K_2CO_3 (1 equiv) in diglyme at 120 °C, a small amount of 9-hydroxy-9-phenylfluorene was formed (entry 3). At 160 °C with the further addition of 2,6-$Me_2C_6H_3CO_2H$ (0.5 equiv), as in the reactions of **1a** and **1b**, the yield of **3a** was improved to 12% (entry 5). Interestingly, $[Cp^*IrCl_2]_2$ was found to be more effective compared to $[Cp^*RhCl_2]_2$ (entry 6 vs entry 5). Furthermore, the Ir-catalyzed reaction proceeded more smoothly in less polar solvents (entries 7−10). Thus, dodecane was the solvent of choice (entry 10). A better result was obtained in the absence of K_2CO_3 and 2,6-$Me_2C_6H_3CO_2H$

dx.doi.org/10.1021/jo4000465 | J. Org. Chem. 2013, 78, 1365−1370

Table 2. Reaction of Triphenylmethanol (3a)[a]



3a 4a

entry	catalyst	solvent	temp (°C)	yield of 4a[b] (%)
1	$[Cp^ERhCl_2]_2$	*o*-xylene	130	0
2	$[Cp^*RhCl_2]_2$	*o*-xylene	130	0
3[c]	$[Cp^*RhCl_2]_2$	diglyme	120	2
4[c]	$[Cp^*RhCl_2]_2$	diglyme	160	4
5[c,d]	$[Cp^*RhCl_2]_2$	diglyme	160	12
6[c,d]	$[Cp^*IrCl_2]_2$	diglyme	160	16
7[c,d]	$[Cp^*IrCl_2]_2$	DMAc	160	4
8[c,d]	$[Cp^*IrCl_2]_2$	NMP	160	4
9[c,d]	$[Cp^*IrCl_2]_2$	mesitylene	160	28
10[c,d]	$[Cp^*IrCl_2]_2$	dodecane	160	33
11	$[Cp^*IrCl_2]_2$	dodecane	160	62 (49)
12	$[Cp^*IrCl_2]_2$	dodecane	170	82 (70)

[a]Reaction conditions: [**3a**]:[catalyst]:[$Cu(OAc)_2·H_2O$] = 0.5:0.01:1 (in mmol), in solvent (3 mL) for 6−10 h under N_2. [b]GC yield based on the amount of **3a** used. Value in parentheses indicates yield after purification. [c]With K_2CO_3 (0.5 mmol). [d]With 2,6-$Me_2C_6H_3CO_2H$ (0.25 mmol).

Table 3. Reaction of Triarylmethanols 3[a]

entry	3	product(s), % yield
1	**3b**, R = Br	**4b**, R = Br, 76
2	**3c**, R = Cl	**4c**, R = Cl, 73
3	**3d**, R = F	**4d**, R = F, 70
4	**3e**, R = CF_3	**4e**, R = CF_3, 76
5	**3f**, R = Me	**4f**, R = Me, 46
6	**3g**	**4g**, 32
7	**3h**, R = CF_3	**4h+4h'**, R = CF_3, 65 (27:73)
8	**3i**, R = Me	**4i+4i'**, R = Me, 57 (38:62)
9	**3j**	**4j+4j'**, 55 (43:57)[b]

[a]Reaction conditions: [**3**]:[$\{Cp^*IrCl_2\}_2$]:[$Cu(OAc)_2·H_2O$] = 0.5:0.01:1 (in mmol), in dodecane (3 mL) at 170 °C for 8 h under N_2. [b]A separable byproduct, 12*H*-dibenzo[*b*,*h*]fluoren-12-one (**5**), was also formed (7%).

5

(entry 11). Finally, the reaction efficiency was considerably improved at 170 °C to produce **3a** in 82% yield (entry 12).

Under the optimized conditions (entry 12 in Table 2), tris(4-substituted phenyl)methanols **3b**−**f** underwent the dehydrogenative cyclization efficiently to produce the corresponding fluorenes **4b**−**f** in 46−76% yields (entries 1−5 in Table 3). In contrast to the case with 2,2-diphenylacetic acids **1**, the alcohols **3** possessing electron-donating groups such as **3f** showed relatively poorer reactivities. Indeed, tris(4-methoxyphenyl)-methanol was completely recovered under the present conditions. In the reaction of (2-methylphenyl)-diphenylmethanol (**3g**), the cyclization took place selectively between two unsubstituted phenyl groups to afford 9-(2-phenyl)fluoren-9-ol (**4g**) (entry 6). The cyclization involving 2-methylphenyl moiety seems to be inhibited by steric factors. In contrast, no preference between unsubstituted and 4-subsituted phenyl groups was observed in the reaction of (4-substituted phenyl)diphenylmethanols **3h** and **3i**: mixtures with statistic distributions were formed (entries 7 and 8). Tris(2-naphthyl)-methanol (**3j**) also underwent the cyclization to give a mixture of two pentacyclic compounds **4j** and **4j′** (entry 9). In this case, a small amount of dehydrogenative cyclization/dehydroarylation[11] product **5** was also detected.

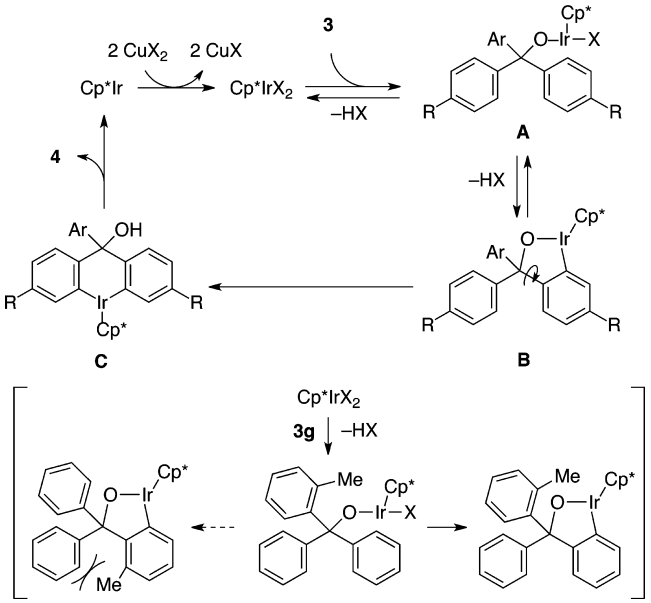
The rhodium-catalyzed cyclization of 2,2-diarylalkanoic acids **1** appears to proceed through steps similar to those in the reaction of 1-amino-1,1-diarylalkanes, which was proposed in our previous communication.[7] The mechanism for the cyclization of triarylmethanols **3** under iridium catalysis is also expected to be essentially similar. A plausible pathway from **3** to **4** is illustrated in Scheme 2. Initial coordination of the hydroxy oxygen of **3** to an iridium center gives a triarylmethoxyiridoum species **A**. Then, hydroxy-directed metalation takes place to form a five-membered iridacycle intermediate **B**. Subsequently, the second cyclomatalation to form a six-membered species **C** and reductive elimination may occur to produce **4**. In the reaction of **3g**, cyclometalation on the 2-methylphenyl ring appears to be suppressed due to the steric repulsion between the methyl group and two phenyl groups.

For providing further mechanistic information, an isotope-labeled triphenylmethanol (**3a**-d_{15}) was subjected to the reaction conditions (Scheme 3). In the early stage, considerable hydrogen incorporations at the *ortho* positions of recovered **3a**-d_n and at the 1- and/or 8-positions of the fluorene nucleus and ortho positions of the 9-phenyl moiety of produced **4a**-d_n were observed. Note that a similar H−D exchange was also observed in the rhodium-catalyzed cyclization of 1-amino-1,1-diarylalkanes.[7] This result indicates that at least the first cyclometalation step to form **B** seems to be partly reversible.

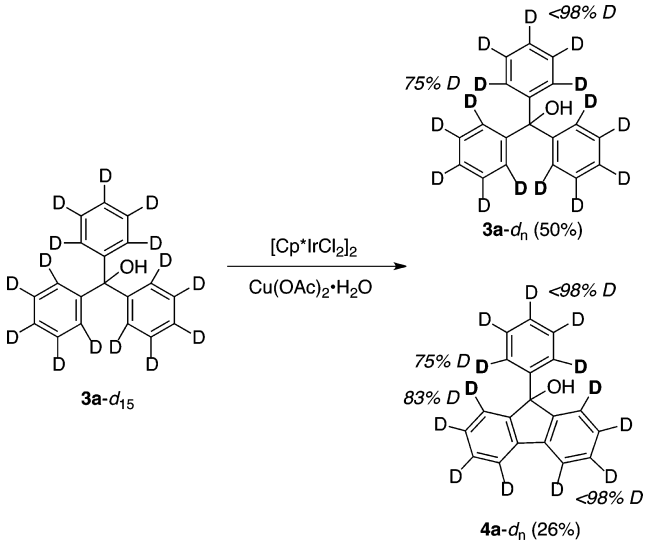
In summary, we have demonstrated that the dehydrogenative cyclization of 2,2-diphenylalkanoic acids and triarylmethanols can be performed effectively under rhodium and iridium catalyzes, respectively. These procedures provide simple synthetic pathways to fluorene derivatives from readily available substrates.

dx.doi.org/10.1021/jo4000465 | J. Org. Chem. 2013, 78, 1365−1370

Scheme 2. Plausible Mechanism for the Reaction of 3



Scheme 3. Reaction of Isotope-Labeled 3a-d_{15}[a]



[a]Reaction conditions: [**3a**-d_{15}]:[{Cp*$IrCl_2$}$_2$]:[$Cu(OAc)_2$·H_2O] = 0.5:0.01:1 (in mmol), in dodecane (3 mL) at 170 °C for 4 h under N_2.

EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by EI using a double-focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC–MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

[Cp^E$RhCl_2$]$_2$,[14] 2,2-diarylalkanoic acids **1b**,[16a] **1d–g**,[16b] and **1h–j**,[16c] and triarylmethanols **3b,e,h**,[17a] and **3d,g,i**[17b] were prepared according to published procedures. Other starting materials and reagents were commercially available.

General Procedure for Cyclization of 2,2-Diarylalkanoic Acids. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 2,2-diarylalkanoic acid **1** (0.5 mmol), [Cp^E$RhCl_2$]$_2$ (0.01 mmol, 8.5 mg), $AgSbF_6$ (0.04 mmol, 14 mg), $Cu(OAc)_2$·H_2O (1 mmol, 200 mg), K_2CO_3 (0.5 mmol, 69 mg), (2,6-$Me_2C_6H_3CO_2H$ (0.25 mmol, 38 mg)), 1-methylnaphthalene (ca. 40 mg) as internal standard, and diglyme (3 mL). The resulting mixture was stirred under nitrogen at 100–120 °C for 20–48 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na_2SO_4. Product **2** was isolated by column chromatography on silica gel using hexane as eluant.

General Procedure for Cyclization of Triarylmethanols. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added triarylmethanol **3** (0.5 mmol), [Cp*$IrCl_2$]$_2$ (0.01 mmol, 8.0 mg), $Cu(OAc)_2$·H_2O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and dodecane (3 mL). The resulting mixture was stirred under nitrogen at 170 °C for 8 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. Purification by column chromatography on silica gel using hexane–ethyl acetate (10:1) as eluent and subsequent gel permeation chromatography gave product **4**.

Procedure for Cyclization of Deuterated Triphenylmethanol. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added triphenylmethanol-d_{15} (**3a**-d_{15}) (0.5 mmol, 138 mg), [Cp*$IrCl_2$]$_2$ (0.01 mmol, 8.0 mg), $Cu(OAc)_2$·H_2O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and dodecane (3 mL). The resulting mixture was stirred under nitrogen at 170 °C for 4 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. Purification by column chromatography on silica gel using hexane–ethyl acetate (10:1) as eluent and subsequent gel permeation chromatography gave product **4a**-d_n and recovered **3a**-d_n. Recovered **3a**-d_n (68.8 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 1H), 7.27 (s, 1.5H). Produced **4a**-d_n (34.7 mg, 26%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 1H), 7.31 (s, 0.34H), 7.37 (s, 0.50H), 7.66 (s, 0.043H).

*9-Methyl-9H-fluorene (**2a**):*[7] mp 43–44 °C, 57 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (d, J = 7.8 Hz, 3H), 3.94 (q, J = 7.8 Hz, 1H), 7.29–7.38 (m, 4H), 7.50 (d, J = 7.3 Hz, 2H), 7.75 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 42.4, 119.8, 124.0, 126.90, 126.92, 140.5, 149.0; HRMS m/z calcd for $C_{14}H_{12}$ (M^+) 180.0939, found 180.0938.

*9-Methoxy-9H-fluorene (**2b**):*[18] mp 44–45 °C, 61 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 3H), 5.61 (s, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.61 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 81.3, 119.9, 125.5, 127.5, 129.0, 141.0, 142.5; HRMS m/z calcd for $C_{14}H_{12}O$ (M^+) 196.0888, found 196.0890.

*9H-Fluorene (**2c**):*[7] mp 113–114 °C, 48 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 2H), 7.28–7.32 (m, 2H), 7.36–7.39 (m, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.79 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.9, 119.9, 125.0, 126.68, 126.70, 141.7, 143.2; HRMS m/z calcd for $C_{13}H_{10}$ (M^+) 166.0783, found 166.0784.

*3-Methyl-9H-fluorene (**2d**):*[19] mp 88–89 °C, 50 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.85 (s, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.26–7.30 (m, 1H), 7.34–7.38 (m, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.60 (s, 1H), 7.76 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 36.5, 119.7, 120.4, 124.7, 125.0, 126.5, 126.6, 127.6, 136.3, 140.3, 141.7, 141.8, 143.6; HRMS m/z calcd for $C_{14}H_{12}$ (M^+) 180.0939, found 180.0940.

*3-tert-Butyl-9H-fluorene (**2e**):* mp 55–56 °C (lit.[20] mp 54–55 °C), 59 mg (53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.86 (s, 2H), 7.26–7.30 (m, 1H), 7.35–7.39 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.80–7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.6, 34.8, 36.5, 116.6, 119.7, 124.1, 124.5, 125.0, 126.5, 126.6, 140.4, 141.6, 141.9, 143.6, 149.9; HRMS m/z calcd for $C_{17}H_{18}$ (M^+) 222.1409, found 222.1406.

*3-(4-tert-Butylphenyl)-9H-fluorene (**2f**):* mp 117–118 °C, 67 mg (45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 9H), 3.93 (s, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.49–7.63 (m, 7H),

dx.doi.org/10.1021/jo4000465 | J. Org. Chem. 2013, 78, 1365–1370

7.84 (d, J = 7.3 Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 34.5, 36.7, 118.5, 119.9, 125.1, 125.2, 125.7, 125.8, 126.76, 126.80, 126.9, 138.7, 140.0, 141.6, 142.0, 142.2, 143.6, 150.2; HRMS m/z calcd for $C_{23}H_{22}$ (M^+) 298.1722, found 298.1724.

*3-Methoxy-9H-fluorene (**2g**):*[19] mp 79−80 °C, 61 mg (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 2H), 3.89 (s, 3H), 6.87 (dd, J = 2.8, 8.2 Hz, 1H), 7.28−7.32 (m, 2H), 7.37 (t, J = 6.4, 7.3 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.1, 55.5, 104.8, 113.2, 119.8, 125.0, 125.5, 126.6, 126.7, 135.3, 141.6, 143.0, 144.3, 159.1; HRMS m/z calcd for $C_{14}H_{12}O$ (M^+) 196.0888, found 196.0890.

*11H-Benzo[a]fluorene (**2h**):* mp 183−184 °C (lit.[21] mp 177 °C), 54 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 2H), 7.28−7.32 (m, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.42−7.46 (m, 1H), 7.49−7.53 (m, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.83−7.90 (m, 4H), 7.97 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.6, 118.7, 119.6, 124.1, 124.9, 125.3, 126.3, 126.4, 126.8, 127.8, 128.9, 130.7, 132.8, 138.9, 139.8, 142.6, 143.3; HRMS m/z calcd for $C_{17}H_{12}$ (M^+) 216.0939, found 216.0938.

*11H-Benzo[b]fluorene (**2i**):* mp 198−199 °C (lit.[19] mp 207−208 °C), 36 mg (33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 2H), 7.32−7.36 (m, 1H), 7.38−7.48 (m, 3H), 7.55 (d, J = 7.2 Hz, 1H), 7.83−7.85 (m, 1H), 7.90−7.92 (m, 3H), 8.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.4, 117.8, 120.6, 123.3, 125.25, 125.30, 125.4, 126.9, 127.5, 127.8, 128.1, 133.0, 133.1, 140.5, 141.1, 141.2, 143.7; HRMS m/z calcd for $C_{17}H_{12}$ (M^+) 216.0939, found 216.0941.

*3,9-Di-tert-butyl-6,12-dihydroindeno[1,2-b]fluorene (**2j**):* mp 246−247 °C, 26 mg (14%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 18H), 3.92 (s, 4H), 7.34 (dd, J = 1.8, 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 2H), 7.84 (d, J = 1.3 Hz, 2H), 7.95 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.7, 34.8, 36.3, 116.2, 116.3, 123.7, 124.5, 140.8, 140.9, 141.8, 142.7, 149.9; HRMS m/z calcd for $C_{28}H_{30}$ (M^+) 366.2348, found 366.2346.

*9-Phenyl-9H-fluoren-9-ol (**4a**):* mp 91−92 °C (lit.[22] mp 90 °C), 90 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 1H), 7.18−7.37 (m, 11H), 7.65 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.6, 120.1, 124.8, 125.4, 127.2, 128.2, 128.4, 129.1, 139.5, 143.1, 150.4; HRMS m/z calcd for $C_{19}H_{14}O$ (M^+) 258.1045, found 258.1050.

*3,6-Dibromo-9-(4-bromophenyl)-9H-fluoren-9-ol (**4b**):* mp 126−127 °C, 189 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 1H), 7.11 (d, J = 8.2 Hz, 2H), 7.15−7.18 (m, 2H), 7.35−7.40 (m, 4H), 7.73 (d, J = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.6, 121.7, 123.6, 123.8, 126.2, 127.0, 131.5, 132.1, 140.2, 140.9, 148.8; HRMS m/z calcd for $C_{19}H_{11}Br_3O$ (M^+) 491.8360, found 491.8362.

*3,6-Dichloro-9-(4-chlorophenyl)-9H-fluoren-9-ol (**4c**):* mp 90−91 °C, 132 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (s, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.21−7.23 (m, 6H), 7.56 (d, J = 1.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.4, 120.8, 125.9, 126.7, 128.5, 129.1, 133.4, 135.5, 139.9, 140.5, 148.5; HRMS m/z calcd for $C_{19}H_{11}Cl_3O$ (M^+) 359.9875, found 359.9879.

*3,6-Difluoro-9-(4-fluorophenyl)-9H-fluoren-9-ol (**4d**):* mp 109−110 °C, 109 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 1H), 6.90−6.97 (m, 4H), 7.21 (dd, J = 5.0, 8.2 Hz, 2H), 7.24−7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.2, 107.7 (d, J = 24.0 Hz), 115.2 (d, J = 21.0 Hz), 115.8 (d, J = 23.0 Hz), 126.1 (d, J = 8.7 Hz), 127.0 (d, J = 8.6 Hz), 138.2 (d, J = 2.9 Hz), 140.5 (dd, J = 2.9, 8.6 Hz), 146.4 (d, J = 2.8 Hz), 162.2 (d, J = 246.3 Hz), 163.8 (d, J = 247.3 Hz); HRMS m/z calcd for $C_{19}H_{11}F_3O$ (M^+) 312.0762, found 312.0766.

*3,6-Bis(trifluoromethyl)-9-(4-(trifluoromethyl)phenyl)-9H-fluoren-9-ol (**4e**):* mp 174−175 °C, 175 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 1H), 7.42 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.0, 117.8 (q, J = 3.8 Hz), 123.8 (q, J = 272.2 Hz), 124.0 (q, J = 272.2 Hz), 125.4, 125.6 (q, J = 3.8 Hz), 125.7, 126.6 (q, J = 3.8 Hz), 130.2 (q, J = 32.6 Hz), 132.4 (q, J = 32.6 Hz), 139.0, 145.2, 153.2; HRMS m/z calcd for $C_{22}H_{11}F_9O$ (M^+) 462.0666, found 462.0663.

*3,6-Dimethyl-9-(4-methylphenyl)-9H-fluoren-9-ol (**4f**):* mp 109−110 °C, 69 mg (46%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.33 (s, 1H), 2.40 (s, 6H), 7.02−7.06 (m, 4H), 7.17 (d, J = 7.7 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.6, 83.0, 120.6, 124.4, 125.3, 128.8, 129.0, 136.6, 138.8, 139.7, 140.6, 148.2; HRMS m/z calcd for $C_{22}H_{20}O$ (M^+) 300.1514, found 300.1512.

*9-(2-Methylphenyl)-9H-fluoren-9-ol (**4g**):*[23] mp 117−118 °C, 43 mg (32%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 3H), 2.33 (s, 1H), 6.95 (d, J = 7.3 Hz, 1H), 7.16−7.24 (m, 5H), 7.34−7.39 (m, 3H), 7.68 (d, J = 7.8 Hz, 2H), 8.32 (d, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 82.7, 120.2, 124.3, 125.7, 126.5, 127.5, 128.6, 129.1, 131.4, 135.1, 140.0, 140.2, 149.3; HRMS m/z calcd for $C_{20}H_{16}O$ (M^+) 272.1201, found 272.1199.

*9-(4-(Trifluoromethyl)phenyl)-9H-fluoren-9-ol (**4h**)*[24] *+ 9-phenyl-3-(trifluoromethyl)-9H-fluoren-9-ol (**4h′**):* 106 mg (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (s, 1H), 7.18−7.48 (m, 10H), 7.64 (t, J = 7.2 Hz, 1.27H), 7.86 (s, 0.73H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.27, 83.31, 117.0 (q, J = 3.8 Hz), 120.2, 120.5, 124.2 (q, J = 272.8 Hz), 124.7, 124.9, 125.09, 125.12, 125.16, 125.21, 125.3 (q, J = 3.8 Hz), 125.8, 127.5, 128.3, 128.6, 129.1, 129.3, 129.39, 129.42, 131.3 (q, J = 32.4 Hz), 138.1, 139.5, 140.2, 142.1, 147.3, 149.7, 150.3, 153.8; HRMS m/z calcd for $C_{20}H_{13}F_3O$ (M^+) 326.0918, found 326.0921.

*9-(4-Methylphenyl)-9H-fluoren-9-ol (**4i**)*[24] *+ 3-methyl-9-phenyl-9H-fluoren-9-ol (**4i′**):*[25] 78 mg (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 1H), 2.39−2.44 (m, 3H), 7.02−7.05 (m, 1.36H), 7.15−7.36 (m, 9H), 7.45 (s, 0.62H), 7.60−7.64 (m, 1.38H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.5, 83.3, 83.5, 119.9, 120.0, 120.7, 124.5, 124.68, 124.71, 125.25, 125.33, 127.1, 128.1, 128.3, 128.4, 128.88, 128.93, 129.0, 129.2, 136.8, 139.0, 139.5, 139.6, 139.7, 140.2, 143.3, 147.6, 150.5, 150.8; HRMS m/z calcd for $C_{20}H_{16}O$ (M^+) 272.1201, found 272.1205.

*12-(Naphthalen-2-yl)-12H-dibenzo[b,h]fluoren-12-ol (**4j**) + 7-(naphthalen-2-yl)-7H-dibenzo[b,g]fluoren-7-ol (**4j′**):* 112 mg (55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (s, 0.43H), 2.82 (s, 0.57H), 7.06 (dd, J = 1.8, 8.7 Hz, 0.43H), 7.11 (dd, J = 1.8, 8.7 Hz, 0.43H), 7.35−7.94 (m, 15H), 8.21−8.22 (m, 1.21H), 8.28 (s, 0.86H), 8.60 (s, 0.43H), 8.86 (d, J = 8.7 Hz, 0.43H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.91, 82.94, 119.2, 122.0, 122.3, 123.5, 123.9, 124.3, 124.35, 124.44, 124.6, 125.8, 125.9, 126.05, 126.09, 126.11, 126.2, 126.5, 126.6, 126.8, 127.4, 127.5, 127.8, 127.87, 127.91, 128.17, 128.22, 128.26, 128.29, 128.59, 128.62, 129.4, 129.5, 130.4, 131.8, 132.5, 132.6, 133.0, 133.1, 133.2, 133.9, 134.2, 134.37, 134.43, 134.7, 137.3, 138.8, 140.6, 141.9, 148.7, 149.3, 149.4; HRMS m/z calcd for $C_{31}H_{20}O$ (M^+) 408.1514, found 408.1512.

*12H-Dibenzo[b,h]fluoren-12-one (**5**):*[26] mp 281−282 °C, 10 mg (7%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.50 (m, 2H), 7.54−7.58 (m, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 8.07 (s, 2H), 8.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.6, 125.7, 126.9, 128.7, 129.0, 130.8, 133.6, 134.3, 137.2, 138.8, 192.8; HRMS m/z calcd for $C_{21}H_{12}O$ (M^+) 280.0888, found 280.0886.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by Grants-in-Aid from MEXT, JSPS, and JST, Japan.

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